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THE STEREOCHEMISTRY OF THE REDUCTION OF ALKYNES

by

Robert Irwin Marston

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THE STEREOCHEMISTRY OF THE REDUCTION OF ALKYNES

A DISSERTATION

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by

Robert Irwin Marston

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A B S T R A C T

The reduction of phenylpropiolic acid with chromous sulfate was followed kinetically and the results showed the reduction to be stereospecifically trans at room temperature. The proposed mechanism accounts for the observed color changes and the slow, rate controlling step is believed to be the transfer of a 3d electron from chromium to carbon.

ACKNOWLEDGEMENTS

The author wishes to express his deepest gratitude to Dr. R. J. Crawford for his guidance in this work.

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I N T R O D U C T I O N

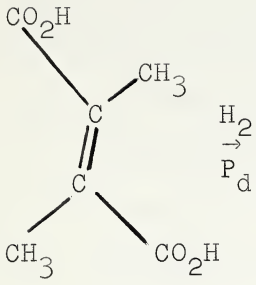
It is possible to reduce alkynes to cis-alkenes by catalytic methods in a stereospecific fashion, but few methods are available by which one may stereospecifically reduce an alkyne to a trans-alkene. Reports in the literature indicate that one of the few methods of homogeneous chemical reduction, by use of Chromium (II), produces the trans-isomer. It is the purpose of this thesis to determine the mechanism by which this reduction occurs and the stereochemical nature of the reduction.

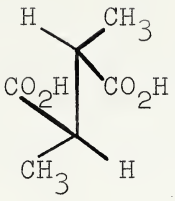
HETEROGENEOUS CATALYTIC HYDROGENATION

The catalytic hydrogenation of phenylpropiolic acid sodium salt with colloidal palladium[1] resulted in the formation of almost exclusively cis-cinnamic acid melting at 68°. Two other cis forms were discovered --- acids melting at 58° and 42°. The isomers melting at the lower temperature were obtained by different methods of crystallization and seeding and appear to be isomorphic with one another. This hydrogenation was carried out at room temperature and atmospheric pressure.

Schwarz and Kelber[2] hydrogenated diphenylacetylene to a mixture of cis and trans stilbenes, predominating in the cis-isomer. Gonzales[3] isolated the lower melting cis isomer from the catalytic hydrogenation of acetylenic acids, and considered the hydrogenation to have no secondary action, and the product to have a predominance of the cis-isomer. Dimethylfumaric acid was catalytically hydrogenated with palladium to 61% meso and 39% d,l-2,3-dimethylsuccinic acid.[4]

1 C.Paal and W. Hartmann, Ber.42 3931 (1909)
2 A.Schwarz and C.Kelber, Ber.45 1949 (1912)
3 A.Gonzales cf. C:A 20 2310 (1926)
4 E.Ott, Ber. 61 2132 (1928)





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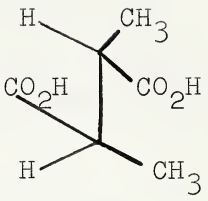

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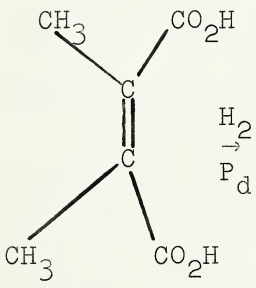

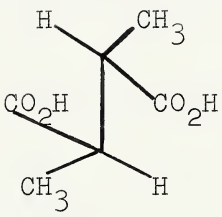

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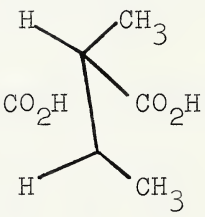


14%

Dimethylmaleic acid was hydrogenated by palladium to 86% meso and 14% d,l-2,3-dimethylsuccinic acid. These reactions by Ott were not checked for isomerization. Cis addition of hydrogen to the dimethylfumaric acid should give the racemate. (The thermodynamically more stable meso compound may have arisen by isomerization after the hydrogenation.)

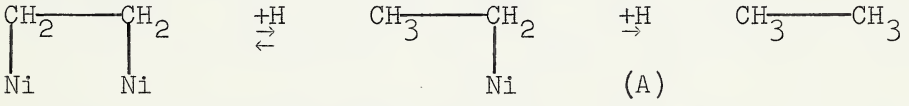
From data available at that time, Bourguel[5] concluded that catalytic hydrogenation of a disubstituted acetylene

5. M. Bourguel, Bull. Soc. Chim France (4) 45 1067 (1929)

compound gave the cis-isomer as the exclusive product. The mechanism suggested by Vavon[6] and Bourguel[7] and developed by Farkas[8] to explain cis-addition of two atoms of hydrogen simultaneously involves three steps:

1. formation of a labile Pd.-H bond.
2. formation of a labile combination Pd-organic-H bond.
3. decomposition of the compound → Pd+ molecule.

A second mechanism developed by Horiuti[9] and Polanyi[10] and confirmed by Twig[11] for the catalytic hydrogenation of ethylene supposes two atoms of hydrogen to be added successively to a catalyst-bound molecule, the rate determining step being the reaction of a van der Waals adsorbed hydrogen molecule



with a chemisorbed ethylene molecule to produce initially an adsorbed ethyl radical and an adsorbed hydro-

6 G.Vavon, Bull.Soc.chim.France (4) 41 1253 (1927)
7 M.Bourguel, Bull.Soc.chim.France (4) 51 253 (1932)
8 Farkas, A. and Farkas,L., Trans.Faraday Soc. 33 837 (1937)
9 I.Horiuti, Trans.Faraday Soc. 30 1164 (1934)
10 M.Polanyi, Trans.Faraday Soc. 35 520 (1939)
11 G.Twig, Diss.Faraday Soc. No.8 152 (1950)

gen atom, and subsequently, a non-adsorbed ethane molecule. (Notice there is non-restricted rotation about the single bond of (A).). Farkas[12] has pointed out that in many cases cis-addition of hydrogen takes place even though the thermodynamically less stable product is formed. Polanyi[10] states this is not proof of the simultaneous addition of a pair of hydrogen atoms since the attachment of the ethylene molecule to the catalyst prior to the formation of the half-hydrogenated state automatically means that cis-addition would occur. Elucidation of this matter was partially accomplished by Romanet[13] with respect to a disubstituted acetylene compound. 1,4-Butynediol was hydrogenated with a Raney nickel catalyst at room temperature and atmospheric pressure. Both cis-and trans-1,4-butenediol were found, as well as butanediol. Cis- trans isomerism was ruled out by distilling cis-butenediol under the same conditions as the hydrogenation product, and attempting to hydrogenate the pure cis-butenediol. (No isomerization was found.) Romanet concludes by saying that trans-butenediol is formed as a primary product of the semi-hydrogenation by a mechanism which remains to be explained. Jenkins and Rideal[14] have examined the

12. A. Farkas, Trans. Faraday Soc. 35 906 (1939)
13. R. Romanet, Compt. rend. 236 1044, 1176, 1679,(1953)
14. G. I. Jenkins and Sir Eric Rideal, J. Chem. Soc. 2490, 2496, (1955).

hydrogenation of ethylene over a nickel catalyst and have shown that chemisorbed hydrogen is capable of adding in a cis mode to ethylene which is not chemically adsorbed on the metal surface. They have also found evidence for the "half-hydrogenated state" at temperatures in excess of 90°. Burwell[15] has recently reviewed the reduction of unsaturated hydrocarbons and reached the conclusion that a carefully prepared catalyst used at temperatures less than 90° gives predominately cis addition to multiple bonds.

HETEROGENEOUS CHEMICAL REDUCTION

Early work done by Straus[16] on the reduction of diphenylacetylene with coppered zinc dust, observed that the predominating product was cis stilbene. Aronstein and Holleman[17] reduced diphenylacetylene to trans-stilbene using zinc dust in acetic acid. Use of a control was not mentioned. They also reduced acetylene dicarboxylic acid to succinic acid, with zinc dust and acetic acid at 60°. Contact period was two days.[18] Neither fumaric nor maleic acid was found but some unchanged acetylene dicarboxylic acid was recovered.

Phenyl propiolic acid was reduced with zinc dust in glacial acetic acid[18], and in alcohol[19] to trans-cinnamic

15 R.L.Burwell, Chem.Rev. 57 895 (1957)
16 F. Straus, Ann. 342 201 (1905)
17 L. Aronstein and A. Holleman, Ber. 21 2831 (1888)
18 L. Aronstein and A. Holleman, Ber. 22 1181 (1889)
19 C. Liebermann and H. Trucksass, Ber. 42 4674 (1909)

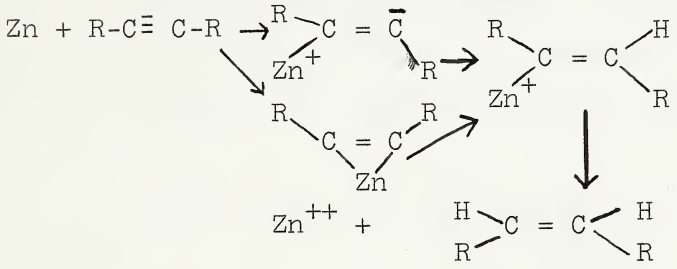
acid. Fischer[20] used zinc dust, 50% acetic acid and a short contact period with platinum to reduce phenylpropiolic acid to trans-cinnamic acid. He found no isomerization of cis-cinnamic acid under the conditions of the reduction period. Partial reduction of acetylenic acids by zinc in acetic acid also formed trans ethylenic acids[3]. Campbell and Eby[21] found no reduction of dibutylacetylene with zinc in acetic acid, zinc in hydrochloric acid or zinc amalgam in hydrochloric acid. Calcium ammonia formed by passing dry ammonia over calcium metal was used to prepare trans-ethylene derivatives of dipropyl, dibutyl, and butylethylacetylene[22]. No control was run.

All work reviewed thus far, with the exception of one case[16], which may well be a heterogeneous catalytic hydrogenation case because of the low activity of copper, seems to involve a trans-reduction.

Burton and Ingold have proposed a mechanism which could be applied to a chemical heterogeneous reduction[23]. Rabinovitch and Looney[24] in 1953 published an article which disputed trans-reduction by a zinc catalyst. They found dideuteroacetylene reduced to cis-deuteroethylene by (a) zinc in hydrochloric acid,(b) copper activated zinc

20. E. Fischer, Ann. 386 374, 394 350 (1912)
21. K. Campbell and L. Eby, J. Am. Chem. Soc.63 216, 2683 (1941)
22. K. Campbell and J. Mc'Dermott, J.Am.Chem.Soc. 67 282 (1945)
23. H. Burton and C.K. Ingold, J. Chem. Soc. 2022(1929)
24. B. Rabinovitch and F. Looney, J. Am. Chem. Soc. 75 2652 (1953).

(c) copper activated magnesium, but found (d) sodium in liquid ammonia and (e) chromous chloride to give trans reduction as expected. They question the validity of calling the heterogeneous reductions chemical, preferring the term catalytic. A mechanism proposed for this type of "pseudo-chemical" reduction is:



It is generally considered that such heterogeneous reductions are of a complex nature and require an intimate knowledge of the metal surface. Since the metal surface is continually changing in this type of a reduction, it is possible that more than one mechanism could be operative, and as a result the complexity of the problem is beyond the scope of this thesis, and may be unsolved for many years hence.

HOMOGENEOUS CHEMICAL REDUCTION

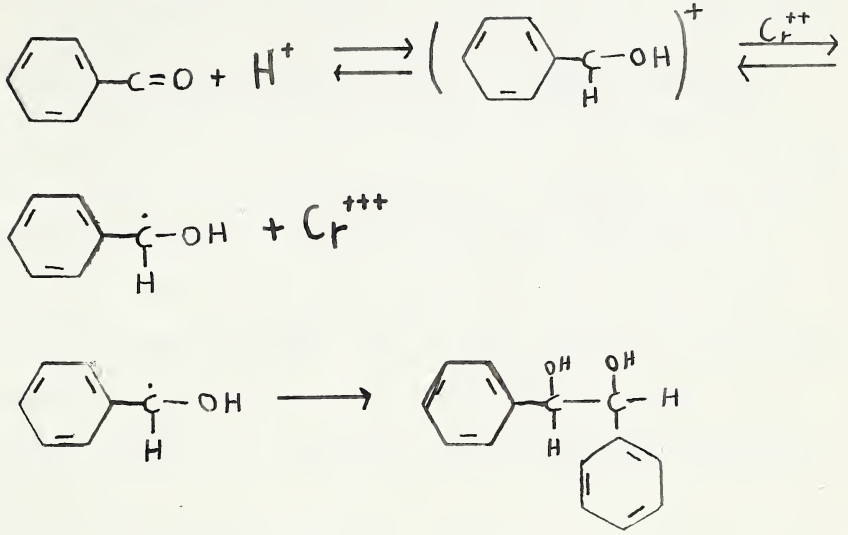
Research on homogeneous chemical reduction has lagged behind that of other types of reduction. Reducing agents in this category are a chromous and vanadous ion and b sodium in liquid ammonia. Berthelot[25] discovered the reducing properties of chromium (II). Since this initial observation, work on chromous ion in acidic media has been sparse. Due to

25. M. Berthelot, Ann (4) 9 401 (1866).

the low solubility of chromous hydroxide the reduction in alkaline media is heterogeneous and thus possibly involves a different mechanism. In 1889, Aronstein and Hollemann[18] obtained trans-cinnamic acid by the reduction of phenylpropiolic acid with sodium in alcohol and also reduced diphenylacetylene to trans-stilbene with sodium in methanol[17], (this reduction may be heterogeneous). Traube and Passarge[26] found chromium (II) at water-bath temperature to reduce fumaric and maleic acids to succinic acid (as determined by melting point) in a 60% yield, but trans-cinnamic acid was found to be unaffected when subjected to the conditions effective upon the two isomeric ethylene dicarboxylic acids. Further experimentation showed that by making the solution alkaline, a 50% yield of β-phenylpropionic acid was produced. Later, Conant and Cutler[27] experimented with chromous chloride on classes of organic compounds not reduced by the more usual soluble reducing agents. They found no reduction of aliphatic or aromatic saturated ketones, aliphatic aldehydes, α, β-unsaturated esters, (acids), alcohols (with some exceptions) and olefins. Their criteria for reduction was the color change from blue chromous to green chromic ion. Many α, β-unsaturated ketones, α, β-unsaturated aldehydes and

26. W. Traube and W. Passarge, Ber., 49 1692 (1916)
27. J. Conant and H. Cutter, J. Am. Chem. Soc., 48 1016 (1926).

aromatic aldehydes were reduced to dimolecular products. The proposed mechanism for the reduction of benzaldehyde is:

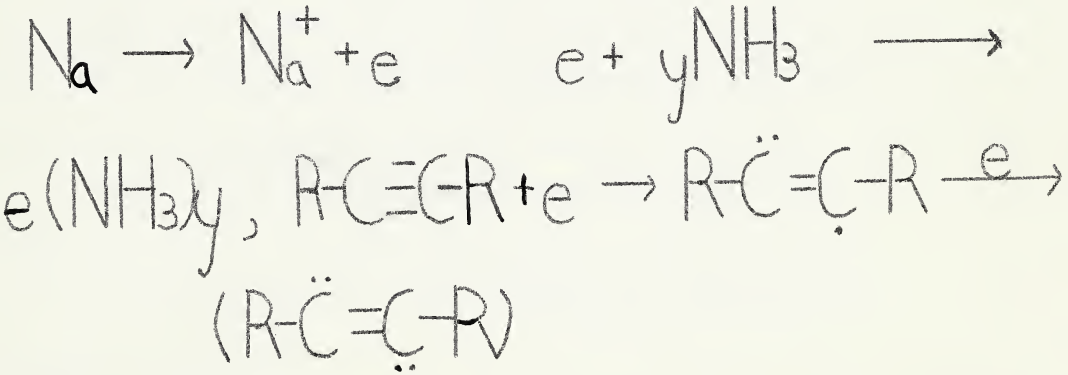


The product, which was seen to precipitate out as two distinctly different types of crystals from the alcoholic chromium (II) reduction of benzaldehyde, was a mixture of meso- and d,l-hydrobenzoin and was identified by oxidation to benzil. Further studies were carried out by Ott and coworkers[28] arriving at a postulate for the observed behavior of the reduction of unsaturated organic compounds which may be stated briefly as the following: the stereochemical course of a reduction changes from cis- to trans- as one uses metals of increasing activity. They found alkaline chromium (II) to reduce phenylpropiolic acid to a mixture predominating in cis-cinnamic acid

28. E. Ott, Ber. 67 1669 (1934)

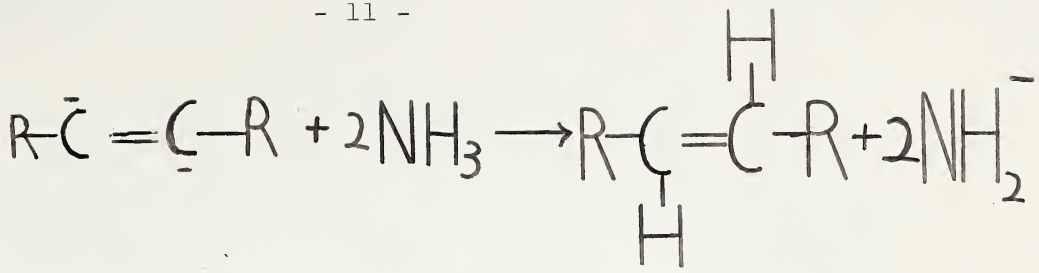
together with some unchanged phenylpropiolic acid in the filtrate while a small amount of trans-cinnamic acid precipitated out of solution at room temperature.

The observation made by Lebeau and Picon[29] that reduction of a monoalkylacetylene linkage by sodium in liquid ammonia stops positively at the formation of the ethylene compound was used by Campbell and Eby[21] in the preparation of monoalkylethylene derivatives. They found also that diamylacetylene was not reduced by sodium in amyl alcohol, but found dialkyl acetylenes to be reduced by sodium in liquid ammonia. The mechanism offered by Greenlee and Fernelius[30] for this reduction is:



In the dicarbanion the electrons repel each other into positions as far apart as possible or trans to one another. This configuration once fixed in the ion persists until after hydrolysis or ammonlysis.

29. P. Lebeau and M. Picon, Compte rend. 159 70 (1914)
30. K. Greenlee and W. Fernelius, J. Am. Chem. Soc. 64 2505 (1942).



Further preparative work was done on monoalkyl acetylenes by Henne and Greenlee[31]. Propyne and 1-octyne were quantitatively reduced by sodium in liquid ammonia. The observation was made that on the addition of ammonium salts, the reduction of dialkyl acetylenes produces a mixture of geometrical isomers, as contrasted with the trans-reduction obtained in the absence of the salt. Rabinovitch and Looney[24] confirmed trans- reduction of dideutero-acetylene bond by chromium (II) or sodium in ammonia. They state that the mechanism of chemical reduction must be stereospecific and possibly involves electron donation to the substrate.

Repetition of much of the earlier work with a proper analysis and isomerism control would be invaluable in the evaluation of the mechanisms proposed for chemical reduction.

Chromium (II) has been used to reduce α-halo-ketones to the parent ketone[32], oxides[33], imide chlorides to imines[34], para nitroaniline, picric acid, and

31. A Henne and K. Greenlee, J. Am. Chem. Soc. 65 2020 (1943)
32. P. Julian and coworkers, J. Am. Chem. Soc. 67 1728 (1945)
33. W. Cole and P. Julian, J.Org. Chem. 19 131 (1954)
34. J. von Braun and W. Rudolph, Ber. 67 269, 1735(1934)

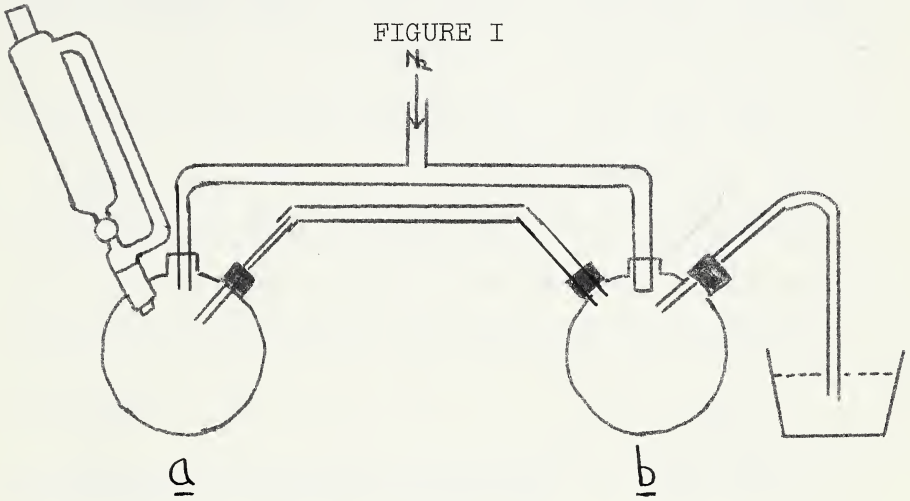
para nitrophenol[35]. Bottei and Furman[36] have used chromous chloride for the quantitative determination of a number of reducible organic compounds. These include anthraquinones, nitro nitroso, azo and acetylenic compounds. All were quantitatively reduced, the nitrogen-containing compounds to the corresponding amines (rupture of the N-N link in the azo compound), the anthraquinone to the corresponding anthrahydroquinone and the acetylenic compound to the corresponding ethylenic compound. They found all the reductions to be complete at room temperature in two minutes.

35. K. Someya, Z. anorg. u. allgem. Chem. 169 293 (1928)
36. R. Bottei and N. Furman, Anal. Chem. 27 1182 (1955)

EXPERIMENTAL

Preparation of Chromous Chloride -- (Method 1) -- Chromous chloride was prepared by a modification of the method used by Walton[37]. Two 3-necked flasks and joining tubing were assembled as in Figure I.

FIGURE I



To flask a was added mossy zinc (50 g. 0.77 moles) and potassium dichromate (10 g. 0.034 moles). An aqueous solution of the monopotassium salt of acetylenedicarboxylic acid (5 g. 0.033 moles) was added to flask b, which contained a magnetic stirring bar. The system was deoxygenated by passing nitrogen gas through flasks a and b. Regulated addition of the concentrated hydrochloric acid brought about the blue chromous chloride color. The chromous chloride was used after being displaced under nitrogen into flask b.

37. H. Walton "Inorganic Preparations", Prentice Hall, Inc., New York, (1948).

Preparation of Chromous Acetate -- Chromous chloride was prepared as indicated previously, then the chromous chloride solution was displaced under nitrogen pressure into the second flask containing sodium acetate (90 g. 1.1 moles) in 80 ml. of water. The precipitate was filtered on a Buchner funnel and washed using deoxygenated water. Care was taken not to expose the precipitate to the atmosphere. Washing was continued with alcohol and finally with ether. The water-free precipitate was then transferred to a glass-stoppered bottle, covered with ligroin and stoppered.

Preparation of Chromous Chloride[38] -- (Method 2) --

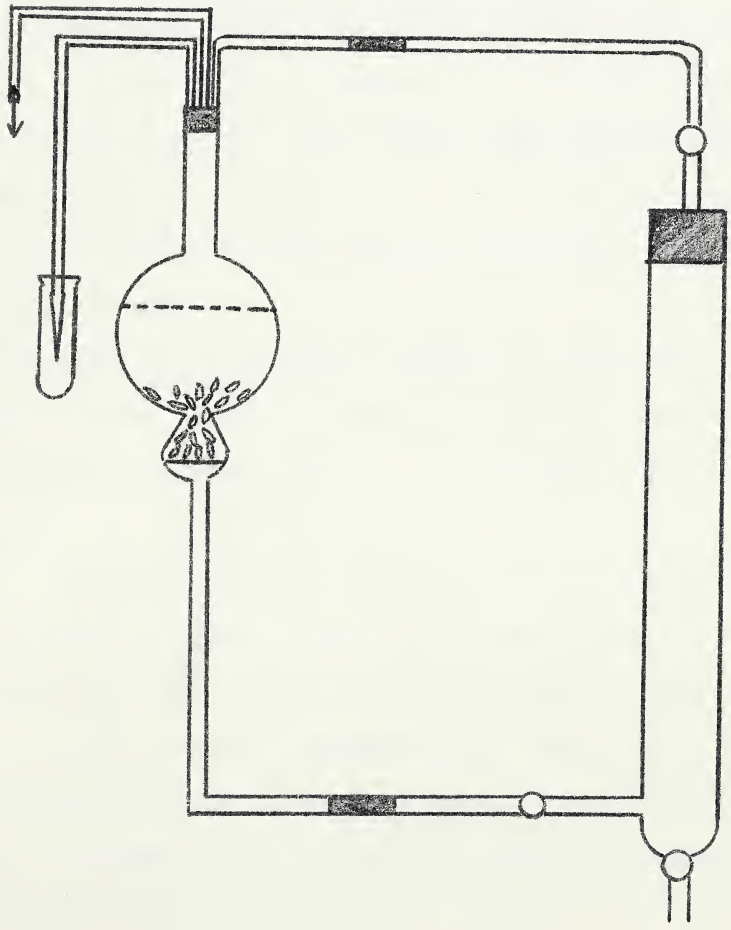
In order to assure freedom from foreign materials such as zinc chloride, chromous chloride was prepared from previously prepared chromous acetate by adding ice-cold saturated hydrochloric acid to the precipitate of chromous acetate in flask b (fig. I). After adding the precipitate to the oxygen-free flask, the red acetate was immediately transformed into a dark blue solution of chromous chloride which was then used as required.

38. D. Hume and H. Stone, J. Am. Chem. Soc.63,1200(1941)

Hume and Stone[38] state that a preparation is free from zinc, and more than 99% of the chromium present is in the divalent state.

Preparation of Chromous Sulfate[39] -- (Method I) -- The apparatus shown in Figure II was blown and assembled.

FIGURE II



39. J. Lingane and R. Pecsok, Anal. Chem. 425(1948)

Amalgamated mossy zinc (500 g. 7.7 moles) was added to the flask. To prepare a 0.1000 N chromous sulfate in 0.1 N sulfuric acid, 29.421 g. (0.1 moles) of pure, dried, potassium dichromate and 500 ml. of water in a two l. erlenmeyer was acidified with 27.8 ml. (0.50 moles) of concentrated acid. A long stem funnel was used to add slowly 75 ml. of C. P. 30% hydrogen peroxide which reduced the dichromate to the chromic ion. This solution was warmed for twenty minutes and transferred when at room temperature to a two litre volumetric and brought to the mark. The storage flask was rinsed and filled with this solution, connected to the nitrogen supply as in Figure II, and flushed with nitrogen.

Preparation of Chromous Sulfate -- (Method II) -- By this preparation it was possible to prepare a chromous sulfate solution containing a minimum of other ions, and store it.

Chromous acetate (71 g. 0.41 moles), prepared as previously described, was added to the flask, as in Figure II, containing a 2 N sulfuric acid solution over 500 g. of amalgamated zinc. The solution was allowed to stand with occasional shaking until all the chromous acetate was converted to chromous sulfate, (about one hour).

Purification of Acetylenedicarboxylic Acid from the Monopotassium Salt[40] --

One hundred and fifty g. of the monopotassium salt of acetylenedicarboxylic acid was dissolved in 240 ml. of water. Sixty ml. of concentrated sulfuric acid was slowly added with stirring. The solution was then extracted with five 100 ml. portions of ether. Evaporation of the ether left pure hydrated crystals of acetylenedicarboxylic acid. The acid was then dried for two days in a vacuum desiccator over concentrated sulfuric acid (m.p. 176°, lit. value 175°).

Precipitation of Maleic and Fumaric Acids by Barium Hydroxide[41] --

A sample of maleic or fumaric acid was neutralized to phenolphthalein using barium hydroxide and then, an equivalent amount of barium chloride was added. The barium salts were precipitated by the addition of four volumes of 95% ethanol to the mixture. After standing an hour, the precipitate was filtered on a coarse sintered glass funnel and washed with 80% ethanol. The precipitate was dissolved directly on the funnel by adding 0.2 N hydrochloric acid and sucked into a clean filter flask. The funnel was washed with the dilute hydrochloric acid, thus affecting a quantitative extraction of maleic and fumaric acids.

40. O. S. Coll. Vol. 2 10 (1943)
41. B. Warshowsky, P. Elving, and J. Mandel, Anal. Chem., 19, 161, (1947)

Attempted preparation of the Dimethylester of Acetylenedicarboxylic Acid[42] --

A mixture of 20 g. of acetylenedicarboxylic acid (16 g. 0.5 moles) of absolute methyl alcohol (35 g. 0.45 moles) of sodium dried A. R. benzene and 7 g. of concentrated sulphuric acid were refluxed for 5 hours, poured into 120 ml. of saturated salt solution, the benzene layer separated and the aqueous phase extracted with three 150 ml. portions of ether. The combined extracts were washed with water, saturated sodium bicarbonate solution (until colorless) and water, then dried with sodium sulfate. The ether and benzene were removed on a water bath under reduced pressure. Distillation of the residue gave 14 g. of product (B. P. 87° at 4 mm. of Hg. lit. value 78.4° at 4 mm. of Hg.) given N_D^{20} 1.4466
found N_D^{20} 1.4777

Preparation of the Dimethylester of Acetylenedicarboxylic Acid --

A modification in the duration of reaction period led to the correct product. The reaction mixture was allowed to stand for several weeks following refluxing. Upon working the product up as previously described, it was found to give (B. P. 78° at 4 mm. of Hg.) N_D^{20} 1.4478, yield 25%.

42. G. Jeffery and A. Vogel, J. Chem. Soc. 678 (1948)

Preparation of the Monamethylester of Maleic Acid[43]

Two moles of methyl alcohol was added to one mole of maleic anhydride at room temperature. Formation of the half ester was rapid and isolation was made by diluting the mixture with water (B. P. 88° at 9 mm of Hg.)

Preparation of the Monomethylester of Fumaric Acid[44]

A g. of fumaric acid was heated with absolute methyl alcohol at 120° until all the acid was in solution. The alcoholic layer separated on standing and was heated with water, then with sodium carbonate until alkaline. Silver nitrate was added until precipitation was complete. The solution was brought to a boil and filtered. The precipitate was washed with water and decomposed with dilute sulfuric acid (M. P. 143 lit. value 144.5).

Preparation of the Monomethylester of Acetylenedicarboxylic Acid

Pure distilled acetylenedicarboxylic acid dimethylester was weighed to three figures and a stoichiometric amount of freshly prepared, standardized, alcoholic potassium hydroxide added slowly with stirring from a burette. The solution turned beet red immediately and a white solid precipitated. This solution was acidified with dilute hydrochloric acid and ether extracted. Evaporation of the ether left an oil, boiling at 90° (4 mm. of Hg.) in an approximately 20% yield.

44. A. Laubenheimer, Ann., 164, 294 (1872)

The infrared spectrum of this half ester indicated a triple bond peak at 2110 cm^{-1}, c = o stretching frequency indicative of an ester at 1725 cm^{-1}, and a wide band in the 2600 cm^{-1} region indicative of carbonyl-OH. The 2110 cm^{-1} peak is not present in the dimethylester and is only found in unsymmetrically substituted acetylenes.

Preparation of Ethyl Cinnamate[45]

In a two litre, 2-necked flask fitted with a short reflux condenser and mechanical stirrer was placed 400 ml. (3.24 moles) of dry xylene and 29 grams (1.26 moles) of clean sodium cut in fine pieces. The flask was heated until all the sodium was molten, then the sodium was stirred rapidly until it solidified. The xylene was poured off and the flask cooled to 0°. Previously distilled, purified, ethyl acetate (455 ml. 4.7 moles) and 4 ml. absolute ethyl alcohol were cooled to 0° and added. To this mixture, kept between 0° and 5° was added 106 g. (1 mole) of benzaldehyde (distilled in vacuo). The addition, with continuous stirring, required about 2 hours. The reaction mixture was stirred for an extra hour then carefully diluted with 95 ml. (1.6 moles) of glacial acetic acid, followed by dilution with water. The water layer was extracted with 50 ml. (0.57 moles) of ethyl acetate. The combined extracts were washed with 300 ml. of 6 N hydrochloric acid and dried with sodium sulfate. The ethyl acetate was distilled from

45. O. S. Coll. Vol. I p. 252

a water bath and the remaining liquid vacuum distilled, collecting from 128° to 133° at (6 mm of Hg.) Yield 70%.

Preparation of Ethyl α, β-Dibromo-β-Phenylpropionate[46]

In a one l. round bottomed flask fitted with an equilibrating dropping funnel was placed the ethyl cinnamate (123 g. 0.73 moles) previously prepared, dissolved in 80 ml. of carbon tetrachloride. The flask was placed on ice and 56 g. (0.7 moles) of bromine was added over an hour with stirring. After standing an hour, the solution was poured into a filter flask, stirred, and sucked dry of bromine and carbon tetrachloride. The caked product was dried by suction on a Buchner funnel and spread on filter paper. Yield of crude product was 87%.

Preparation of Phenylpropiolic Acid[47]

Potassium hydroxide (154 g. 2.7 moles) was dissolved in 730 ml. of 95% ethanol by heating on a steam cone. To the cool alkaline solution was added the crude ethyl α, β-dibromo-β-phenylpropionate. After the initial reaction, the mixture was refluxed for five hours on the steam cone. The reaction mixture was cooled and the salts separated by filtration. The filtrate was treated with concentrated hydrochloric acid until neutral to litmus and the precipitated salts again filtered by suction. The filtrate was distilled to 95° and the residue, combined

46. O. S. Coll. Vol. II p. 270
47. O. S. Coll. Vol. II p. 515

with the salts, was dissolved in 500 ml. of water and the cooled solution was immersed in an ice-salt bath and stirred vigorously while dilute sulfuric acid was added dropwise from a dropping funnel. After precipitation was complete, the solution was filtered, washed with 50 ml. of a 2% sulfuric acid solution and washed with water. The acid was dissolved in a 5% sodium carbonate solution and ether extracted. The sodium carbonate solution was treated with 20 g. of norite, and heated on a steam bath for an hour, filtered and cooled to 0° in an ice bath. After the addition of 600 g. of ice the acid was stirred very vigorously during the dropwise addition of dilute sulfuric acid. The precipitate was filtered, washed with 2% sulfuric acid and then with water, air dried and recrystallized in small portions from carbon tetrachloride. (M. P. 137; lit. value 137).

Preparation of α, β-Dibromo-β-Phenylpropionic Acid[48]

Cinnamic acid (74 g. 0.5 moles) was dissolved in 500 ml. of carbon tetrachloride in a 3 neck round bottom flask fitted with a condenser, stirrer and separatory funnel. This solution was brought to a boil, stirred vigorously, and 79.9 g. (1 mole) of bromine in 50 ml. of carbon tetrachloride was added over a period of 45 minutes. Stirring was continued

48. M. Reimer. J. Am. Chem. Soc. 64 2510 (1942)

while cooling until the product separated. The product was filtered, dried and weighed. Yield was 93% (M. P. 191° lit. value 195°). This product was then dehydrohalogenated as in the previous preparation.

Preparation of cis (68°) Cinnamic Acid[1]

cis-Cinnamic acid was prepared by the hydrogenation of the sodium salt of phenylpropiolic acid using Lindlar's catalyst. Sodium phenylpropiolate (24 g. 0.143 moles) and 1 g. of Lindlar's catalyst were added to 150 ml. of water in a hydrogenation flask. The hydrogenation was complete in about 6 hours after which the solution was filtered, acidified ether extracted, and evaporated to dryness. The precipitate was dissolved in 5% sodium carbonate, steam distilled, filtered acidified and again ether extracted. Evaporation of the ether left a yellow oil from which crystals of cis-cinnamic acid were induced by scratching with a stirring rod. The crystals were purified by using a small volume of low boiling petroleum ether in which trans-cinnamic acid is nearly insoluble. (Yield 17%. M. P. 67°; lit. 68°)

Preparation of Lindlar's Catalyst[49]

Fifty g. of the purest precipitated calcium carbonate was stirred with 400 ml. of water. To this solution was added 50 ml. of palladium chloride solution containing 5% palladium. The solution was stirred for 5 minutes at 25° and for 10 minutes at 80°.

49. H. Lindlar, Helv. Chem. Acta 35 450 (1952)

The hot suspension was shaken with hydrogen in a hydrogenation apparatus until no more hydrogen was adsorbed. The solution was filtered and washed with water, then stirred vigorously in 500 ml. of water. Five g. of lead acetate in 100 ml. of water was added and the mixture stirred for 10 minutes at 20° and for 40 minutes at 90°. The solution was again filtered, washed and dried at 45° in a vacuum dessicator.

Reduction of Phenylpropiolic Acid

The phenylpropiolic acid was reduced using the apparatus shown in Figure I. The reduction of potassium dichromate was carried out as previously described and the resulting chromous salt solution forced into the second flask containing 3.5 g. (0.024 moles) of pure phenylpropiolic acid dissolved in a 50% water-glacial acetic acid mixture. After standing twelve hours, the mixture was filtered and the precipitate washed with 10 ml. of 2% sulfuric acid. This product melted at 132° - 133.5° and was recovered in a 93% yield. The amide was prepared by the method of Schriner and Fuson[50] (M. P. 146° lit. value 147° for cinnamide). The melting point of a mixture of the product with trans-cinnamic acid showed no depression.

Test for Isomerization of cis-Cinnamic Acid

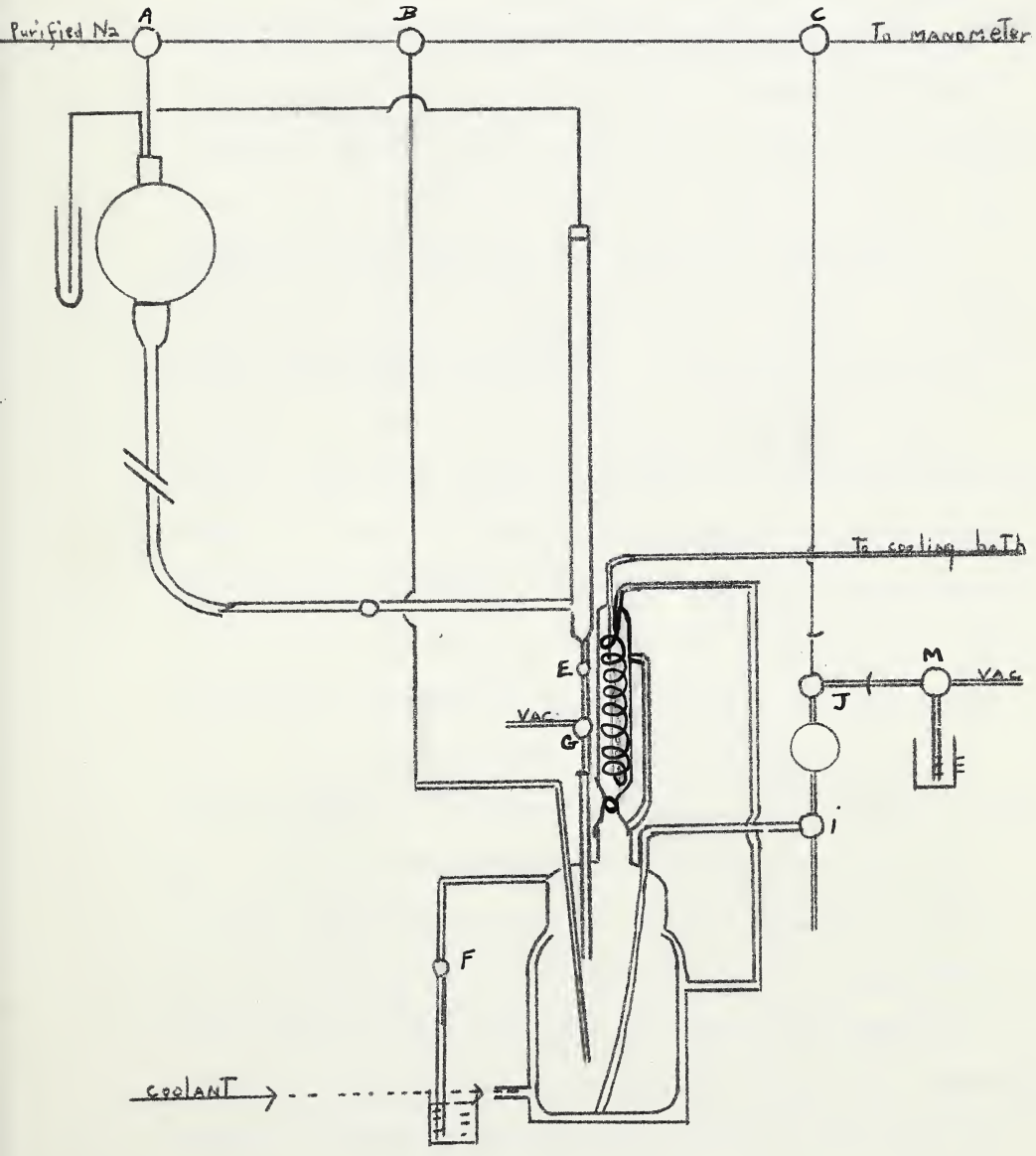
A control was run using cis-cinnamic acid (M. P. 52°) in place of the phenylpropiolic acid described in the previous experiment. The cis cinnamic acid was recovered unchanged after being subjected to the reaction conditions (yield 92% M. P. 52°)

50. R. Shriner, R. Fuson, D. Curtin "The Systematic Identification of Organic Compounds", Fourth Ed., John Wiley & Sons, Inc., New York, 1956, P. 200

Kinetic Measurements

The reduction was then followed by using the apparatus illustrated below.

FIGURE III



The reaction vessel and dropping funnel were kept at 0.2° by water circulated into the bottom of the jacket, out the top and through the glass coil in the dropping funnel. Purified nitrogen was passed through the system and solution to insure freedom from oxygen. The normality of the chromous sulfate was known to a close approximation beforehand and the molarity of the phenylpropiolic acid was prepared such that the final normality of the chromous sulfate would still use enough 0.045 normal potassium dichromate to activate the titrator. The volume of the sampler was 8.04 ml., therefore a final normality of 0.05 would use 8.93 ml. of standard potassium dichromate. A 1/3 total volume of glacial acetic acid was found to keep the organic acid in solution (trans-cinnamic and phenylpropiolic) while it was not concentrated enough to precipitate out chromous sulfate. Because the volume was 60 (+) ml., a total volume of 180 ml. of solution was used. The amount of phenylpropiolic acid to be added was then calculated from the volume of approximately known normality chromous sulfate. This weight (1.72 g. 0.0118 moles) of phenylpropiolic acid was dissolved in 50 ml. of glacial acetic acid and 10 ml. of water (to prevent the glacial acetic acid from freezing at 0.2°) and added to the equilibrating dropping funnel. To the flask was added the remaining volume of glacial acetic acid (10 ml. 0.167 moles)

50 ml. of water and finally enough water and glacial acetic acid for four standardization titrations of chromous sulfate and still leave 50 ml. of water and 10 ml. of glacial acetic acid in the flask together with the 60 mls. of chromous sulfate. The total volume of solvent and reactants added to the flask was 62.86 ml. of water, 13.22 ml. of glacial acetic acid and 76.08 ml. of chromous sulfate solution.

Precautions which must be observed when using a system which is open to the atmosphere both on pressure and on vacuum is that a standard procedure of checking be adopted for the line valves. Another necessary precaution to insure accurate titration values was to clean the electrodes with acetone after each titration and that the titrator be well-grounded. To insure a good value, the solution was allowed to stand only a minimum time interval between sampling and titration.

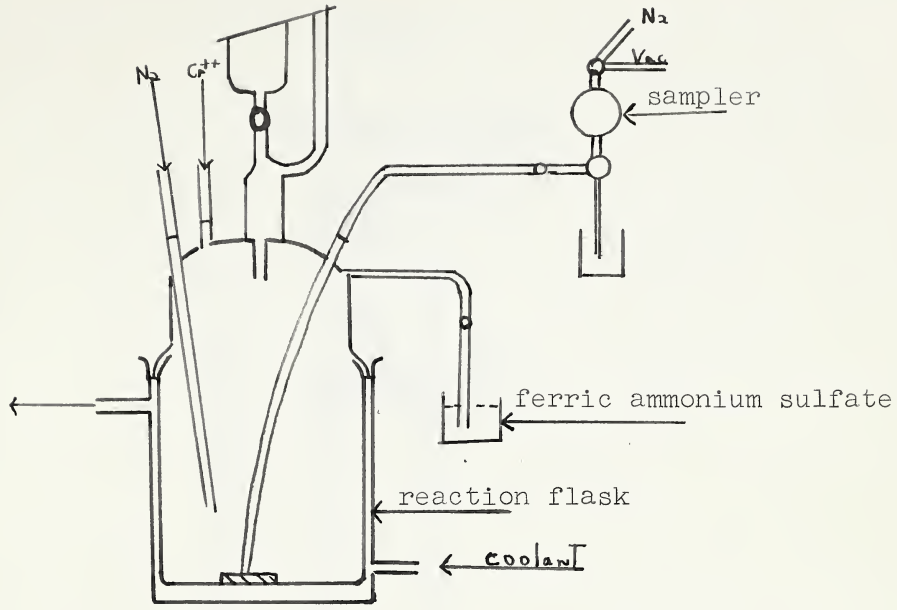
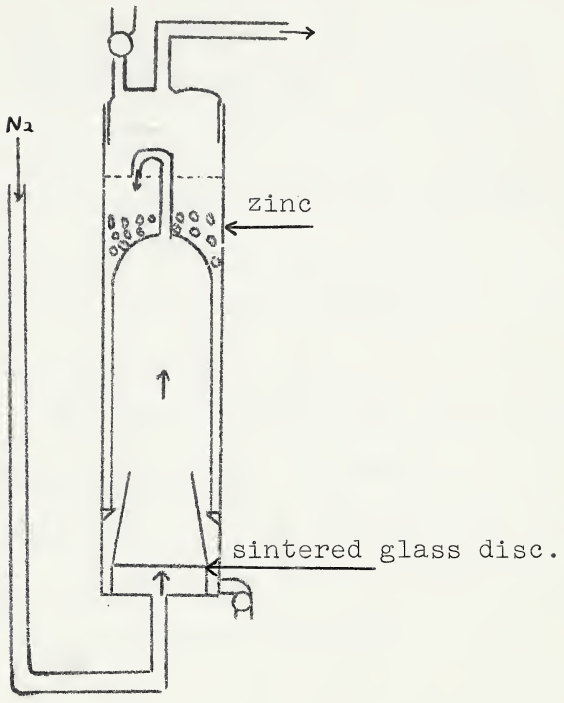


FIGURE IV

The reaction vessel illustrated was constructed from a ball and socket 102/75 ground glass joint. The male joint was closed at one end and sealed into a one l. beaker provided with inlet and outlet nipples. Into the female portion of the joint were sealed three 10/30 female joints, one female 24/10 joint and a 8 mm. outlet. The sampler tube was gently curved and reached to the bottom of the flask. The sampler was constructed from two, three way stop cocks with a spherical bulb between them. The joint between the sampler and the flask is a ball and socket as is the joint between the top of the sampler and the vacuum line. A tygon line was used to connect the vacuum to the top of the sampler.

FIGURE V

Nitrogen Scrubber



The sintered glass disk serves to break the nitrogen gas into a very fine steam of bubbles. The bubbles pass up the sleeve and come out the downward displacing outlet leaving the liquid behind and promoting circulation of the chromous sulfate.

Preparation for a Run

The water bath was cooled to approximately 0° by adding ice, and maintained at 0.2° by circulating a 50% mixture of alcohol and water through copper tubing in the bath and through more copper tubing in an ice salt mixture from a reservoir in

the same ice salt mixture. The alcohol-water circulation was maintained by a thermostatically controlled pump. The proper amount of water and glacial acetic acid was added to the reaction flask together with a stirring bar. The flask was capped and the lines were inserted. The dissolved phenylpropiolic acid was poured into the equilibrating dropping funnel and the rest of the apparatus assembled. The flask, sampler and lines were evacuated, taking precautions to have c closed to the sampler. Scrubbed nitrogen was passed into the system taking precaution to close b to the reaction flask and open c to the sampler. At all times during the evacuation the entire system was kept closed to the atmosphere and water outlets. This condition also holds for filling the system until atmospheric pressure is reached (as evidenced by the monometer) then line f was opened to water. This procedure of evacuation and filling was repeated several times then 76.08 ml. (.041 moles of chromous sulfate was added from the burette and four samples were taken.

Sampling

This was done by a nitrogen flow down b into the reaction flask, forcing solution out the sample tube; opening i to the flask and sampler; opening j 3 ways and opening m to j and the atmosphere via

water. j was closed to the sampler as soon as the sampler was full, b was opened 3 ways and the bottom tube of the sampler was placed in the beaker containing the 0.5 molar ferric ammonium sulfate. i was opened to sampler and beaker then j was opened to nitrogen and sampler.

Discharge under a slight pressure insured a clean delivery each time. The four samples were titrated with standard potassium dichromate using a "Sargent-Malmstadt Automatic Titrator". Having established the initial normality by multiplying the standardization normality by 2/3, and given the chromous sulfate time to come to the temperature of the cooling bath, the contents of the dropping funnel were added to the flask and simultaneously, the timer was started. Samples were taken from the flask in the same manner as for the standardization, run into the 0.5 molar ferric ammonium sulfate and titrated with the standard potassiumdichromate. The time of each sample taken was noted when the half of the sample was in the ferric ammonium sulfate solution. The number of samples was governed by the volume of solution in the flask and expediency of taking them governed by the half-life of the reaction. At 0.2° the reduction had a half-life of 27.2 minutes therefore sampling was spread over about an hour, although the first 3 or 4 samples were taken as rapidly as possible to follow any induction period.

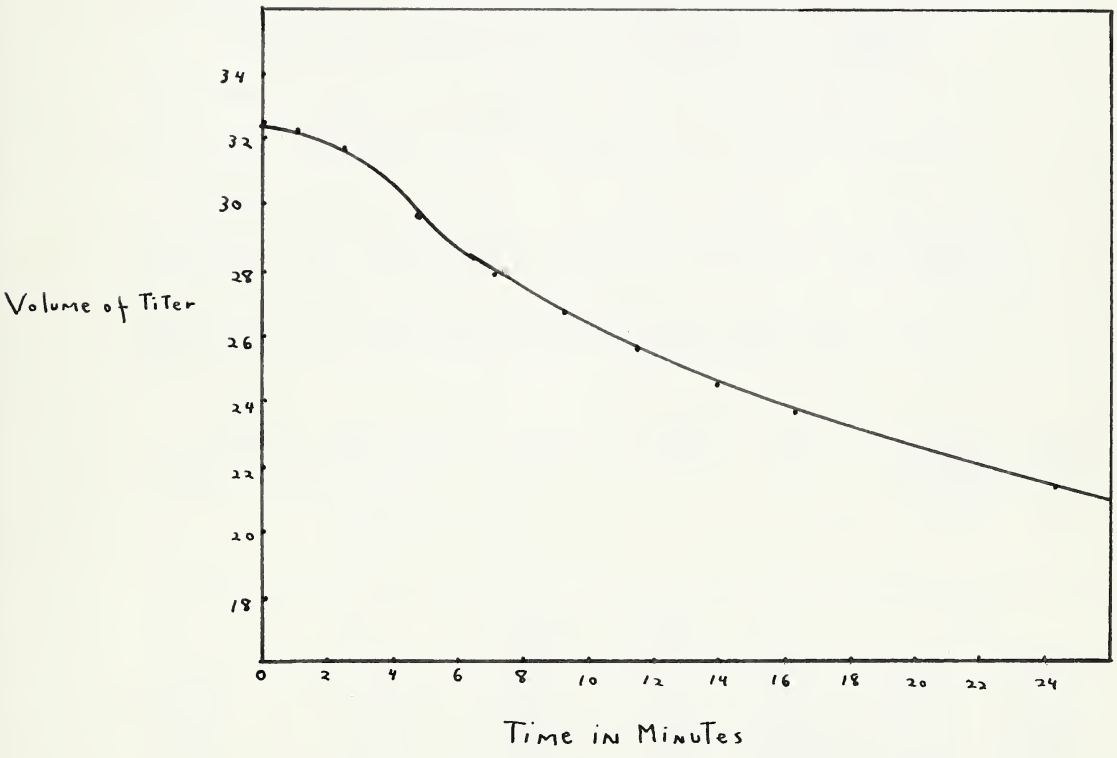
A Kinetic Run

The total volume in the flask was 180 ml. made up of 60 ml. 0.181 N chromous sulfate, 60 ml. of water and 60 ml. of glacial acetic acid. The calculated initial titre from the standardizations was 32.6 ml. of 0.045 N potassium dichromate. Temperature of reactants was +0.2° and weight of phenylpropiolic acid added was 1.72 g.

Time (in seconds)	Titer. (in ml.)
0.0	32.6
60	32.3
148	31.75
285	29.70
420	27.90
550	26.75
686	25.70
835	24.60
980	23.70
1462	21.50
2174	19.20
3053	17.40

Temperature was controlled to $\pm \frac{5}{100}$ of a degree.

The graph of volume V. S. time illustrated shows what may be an initiation period.

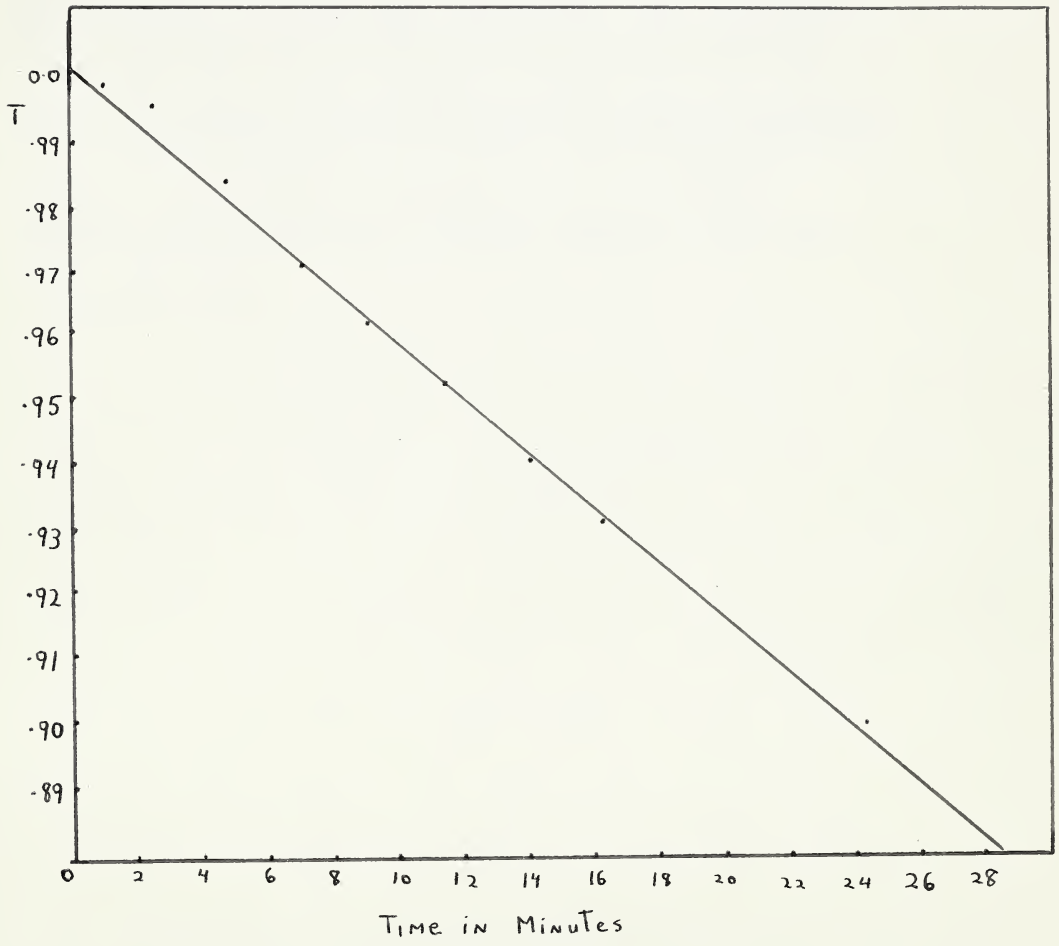


The order of this reaction was then found by plotting the proper values in the various rate equations. A straight line was found for the plot of a second order rate equation, and the values are tabulated below where a = initial phenylpropiolic acid concentration and b = initial chromous sulfate concentration. Both values are in moles per liter.

The rate expression $t = \frac{2.303}{k(2a-b)} \log \frac{b(a-x)}{a(b-2x)}$ was used, where a, and b are as defined above, and x is the concentration in moles per liter of phenylpropiolic acid which has reacted at time t. The rate constant was obtained by plotting time vs. $\log \frac{b(a-x)}{a(b-2x)}$ and the rate constant k was derived from the slope.

Time (min./100)	Initial titer minus titer	a-x	b-2x	2x	$\frac{b(a-x)}{a(b-2x)}$ (M)	log of M
0	0	0.0655	0.181	0	1	0
1	0.3	0.0647	0.179	0.0017	0.9965	-.0015
2.47	0.85	0.0631	0.176	0.0047	0.9894	-.0046
4.75	2.90	0.0575	0.165	0.0161	0.9638	-.0160
7.0	4.70	0.0524	0.155	0.0262	0.9356	-.0289
9.17	5.85	0.0492	0.148	0.0326	0.9162	-.0380
11.45	6.90	0.0462	0.142	0.0386	0.8966	-.0474
13.95	8.00	0.0431	0.136	0.0447	0.8470	-.0585
16.33	8.90	0.0406	0.131	0.0498	0.8549	-.0681
24.30	11.10	0.0345	0.119	0.0620	0.8013	-.0962
36.23	13.40	0.0280	0.106	0.0750	0.7302	-.1366
59.0	13.30	0.0230	0.096	0.085	0.6569	-.1825

A plot of log $\frac{b(a-1/2X)}{a(b-x)}$ vs. time is shown below.



Log M

The slope of this line was multiplied by $\frac{2.303}{2(a-b)x60}$ to find the reaction rate. $k = 3.16 \times 10^{-3}$ litres moles^{-1} sec.$^{-1}$

A kinetic run was made at 16° with a calculated excess of chromous sulfate, and this mixture was allowed to stand for ten hours. The titer of this solution agreed satisfactorily with the end point calculated from the weight of phenylpropiolic acid. The decrease in molarity of a chromous sulfate upon standing the same length of time was corrected for.

Recovery of the reduction of the monopotassium salt of acetylenedicarboxylic acid by acidification and ether extraction proved unsuccessful. Recovery by evaporation of the reduction mixture also proved unsuccessful. Precipitation of chromic hydroxide followed by treatment of the filtrate with barium hydroxide and barium chloride uncovered no organic compound. The possibilities of using an ion exchange column were investigated. Cation exchange was deemed unfeasible because of pH difficulties.

The column is regenerated at the pH of the solution and chromic hydroxide precipitates in the pH range that the IR 120 resin operates. Precipitation of the chromium ion and anion exchange using IRA 400 was unsuccessfully attempted.

The possibilities of using a compound which was polar enough to be slightly water soluble yet very soluble in organic solvent led to the preparation of the monomethyl ester of acetylenedicarboxylic acid. The yield was too poor and the preparation too time consuming to be considered as a feasible compound to study.

Phenylpropiolic acid was investigated as a suitable compound to reduce. Glacial acetic acid was found to be the best suited solvent. Ethyl alcohol was found to esterify with the reduced phenylpropiolic acid under the conditions of the reduction. An attempt to follow the reduction potentiometrically gave results which were not reproducible. Several of the

problems encountered here were

$$2\ Cr^{++} + 2H^{+} \rightarrow 2\ Cr^{+3} + H_2 \quad ,$$

in the presence of platinum, coating of the electrodes with precipitated organic material and a rapidly changing hydrogen ion concentration. Controls showed that the potential changed with time.

DISCUSSION OF RESULTS

The equation for the reduction is:

$$2\ Cr^{++} + 2\ H^{+} + C_6H_5 - C \equiv C - CO_2H \rightarrow$$

$$2\ Cr^{+++} + \begin{matrix} H \\ \diagdown \\ C \\ \diagup \\ C_6H_5 \end{matrix} = C \begin{matrix} \diagup\ CO_2H \\ \diagdown\ H \end{matrix} \qquad (1)$$

The hydrogen ion is kept relatively constant by using glacial acetic acid as a cosolvent.

Stereochemistry of the Reduction

Trans-Cinnamic acid was isolated from the reduction mixture as a precipitate in 93% yield. Cis-cinnamic acid was subjected to the same reaction conditions as was phenylpropiolic acid, to see if the thermodynamically less stable cis-acid could have isomerized under these conditions.

No precipitate of trans-cinnamic acid was observed on standing and ether extraction of the mixture gave a 92% yield of a compound identified as cis-cinnamic acid by mixture melting point. Ott[28] recovered a mixture of unchanged phenylpropiolic acid, cis and trans and hydrocinnamic acids from an alkaline chromous ion reduction at room temperature. No evidence of any organic acid other than trans-cinnamic was found in the reduction mixture.

Characteristics of the Reactions

The reduction at 0.2° displayed several color changes before the characteristic chromic green was observed. Immediately after the addition of phenylpropiolic acid dissolved in glacial acetic acid, a momentary light green color was apparent which was superceded by a reddish brown which remained for about 15 minutes, gradually turning a deeper shade of brown which melded into dark green.

Mechanisms

The mechanism proposed by Conant and Cutter[27] for the chromous ion reduction of benzaldehyde (see page 8) involves the addition of a proton to the carbonyl to form an oxonium cation. This cation then gained an electron from the chromous ion to form a free radical and the chromic ion.

i.e. $R\text{-}\overset{H}{\underset{H}{C}} = O + H^{+} \rightleftarrows$

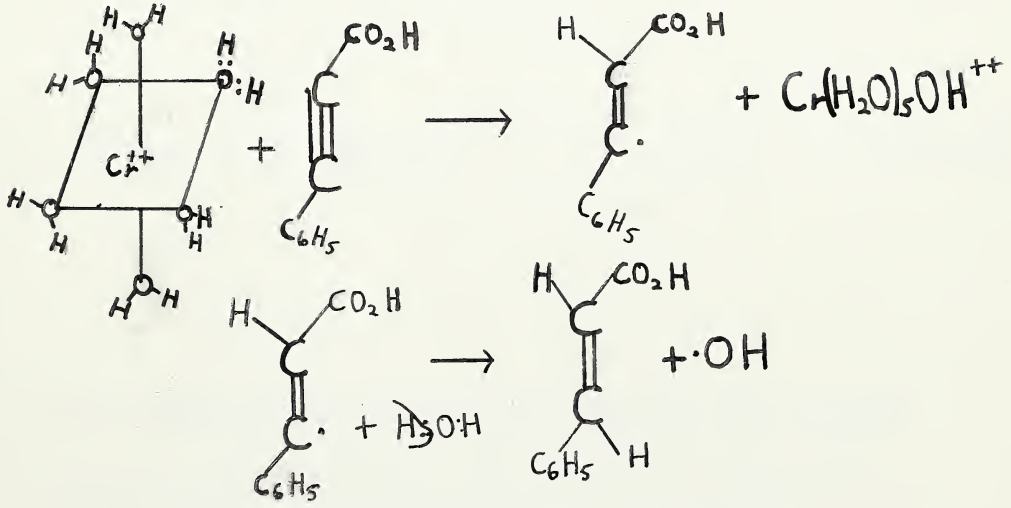
$R - \overset{H}{\underset{H}{C}} - \overset{+}{O}H \quad \overset{Cr^{++}}{\rightleftarrows} \quad R - \overset{H}{\underset{\bullet}{C}} - OH \quad \overset{\text{dimerizes}}{\rightarrow}$

The free radical then dimerized to form hydrobenzoin.

Farkas and Farkas[8] believed chemical reduction to proceed by a stepwise mechanism; the intermediate formed by the addition of the first atom, adjusting itself to a position of minimum potential energy before the second addition step.

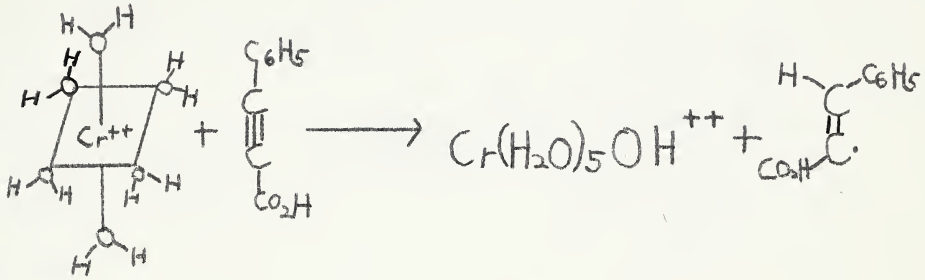
Greenlee and Fernelius[30] postulated the stepwise addition of two electrons from the ionized solvent to the triple bond, which then rearranged to a <u>trans</u> dicarbanion before ammonolysis (see p. 10).

Some other mechanisms proposed for the homogeneous chemical reduction of an acetylenic bond are:



The .OH stabilizes by transfer of a 3d electron from chromium

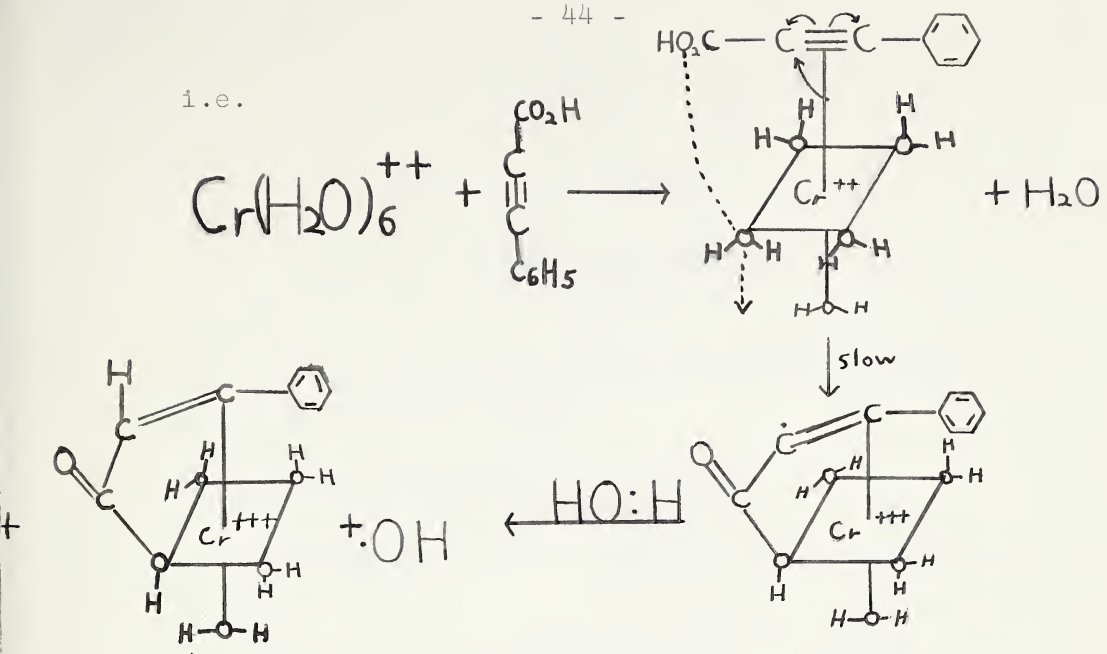
(b) The other facet of this mechanism would involve an attack at the other end of the multiple bond.



$$\cdot OH + Cr(H_2O)_6^{++} \longrightarrow OH^- + Cr(H_2O)_6^{+++}$$

(c) Another mechanism proposed involves the displacing of a complexed water molecule by the phenylpropiolic acid to form an unstable intermediate.

i.e.

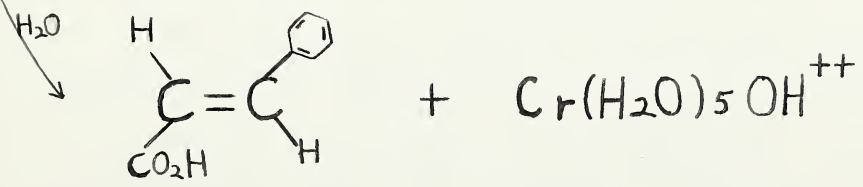


Here the chromium has donated a 3d electron to form a direct bond with the carbon.

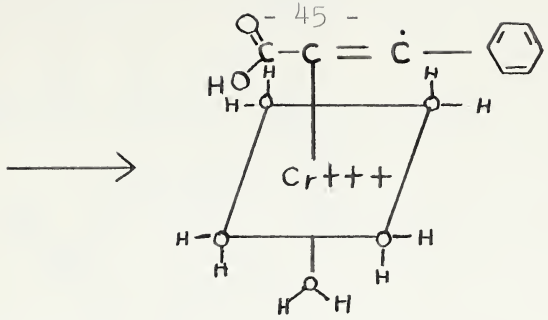
The .OH reacts with $Cr(H_2O)_6^{++}$ as before

$$\rightarrow OH^- + Cr^{+++}\ (H_2O)_6$$

and the carbide bond is hydrolyzed



(d) $Cr(H_2O)_6^{++}$ + Acid → reactive intermediate



This free radical then follows the course outlined for mechanism c.

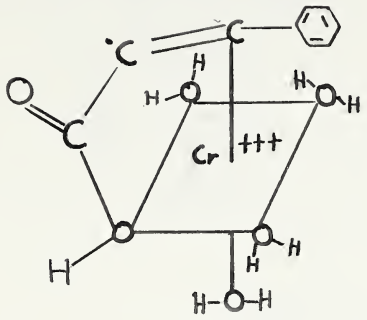
Elucidation of Proposed Mechanisms

Conant and Cutter's mechanism will not be considered because it involves a carbonyl addition. The mechanism of Farkas and Farkas is in essence similar to mechanisms a to d, the difference being that their intermediate does not include the reducing agent, and they only explain the stereochemistry of the reduction. No mention is made of how the hydrogen atoms are produced or transferred to the reaction site, for if the hydrogen atoms are produced before the rate determining step, one could expect a chromous solution to rapidly evolve hydrogen in aqueous media.

The mechanism of Greenlee and Fernelius is not feasible for the reduction in acid solution, because it postulates the existence of a dicarbanion. The energy of activation for a reaction involving a dicarbanion would be much larger than observed characteristics of this reduction.

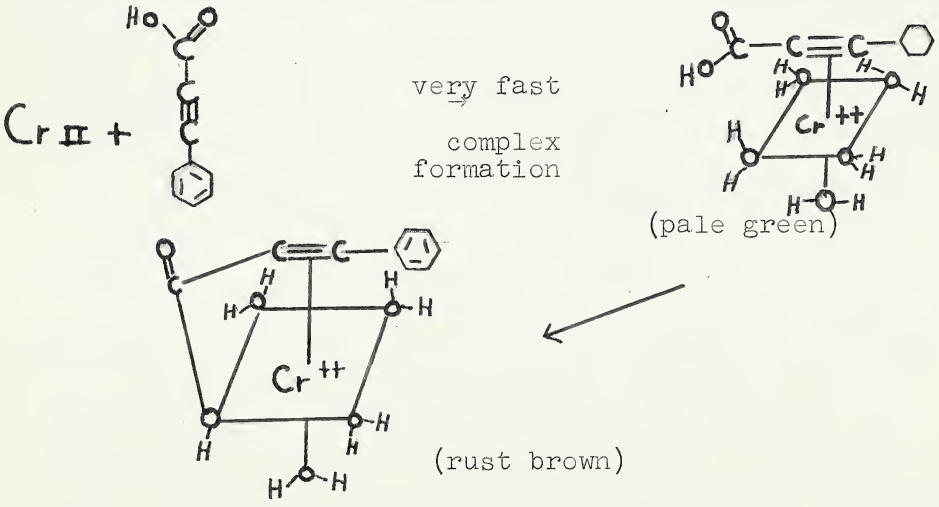
Mechanisms a and b do not explain color changes observed during the course of the reduction, c and d do. Mechanism c is favored over mechanism d because

this type of structure may be written,



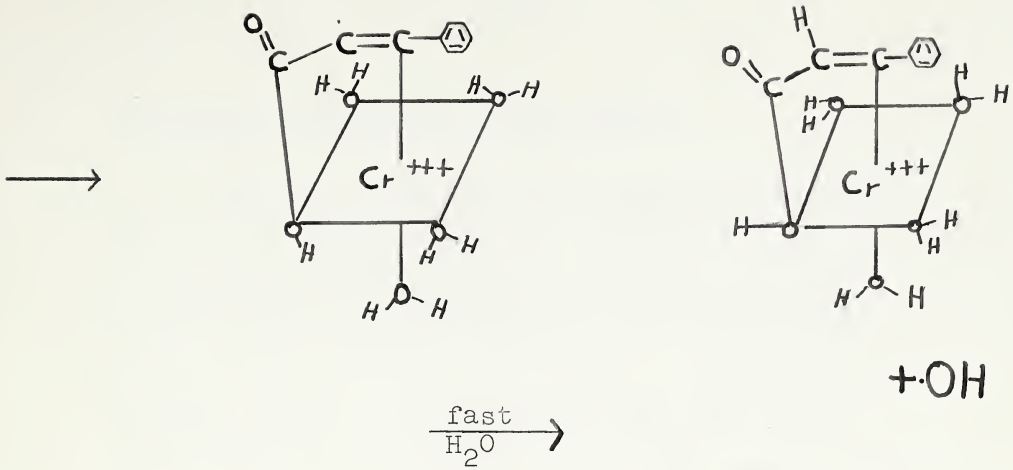
whereas mechanism d involves a 4-membered ring, and does not explain trans-reduction. Evidence for the existence of a benzyl chromium compound[51] supports this postulated chromium - carbon bond.

The proposed mechanism for this reduction is:



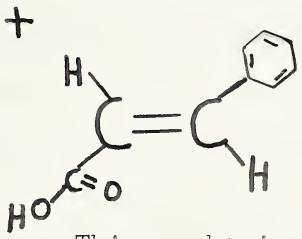
slow rate determining step (transfer of a 3d electron from chromium to carbon).

51. F. Anet and E. Leblanc, J. Am. Chem. Soc. 79 2649 (1957)



fast
H_2O

$Cr(H_2O)_5OH^{++}$ ← fast cleavage of carbide bond



trans-cinnamic acid

This mechanism explains the color changes observed, the stereospecifically trans-reduction and of the mechanisms considered seems to best fit the reduction.

Proposals for Further Investigation

Further insight could be gained into the kinetics of this reduction, and more concrete evidence for its mechanism by using deuterium oxide. The reaction would give evidence of an isotope effect if it was following the course postulated by mechanism a or b. The rate of disappearance of c≡c could be followed spectrophotometrically to establish its order. Other studies which might cast more light on the reduction would be a change of solvent, and concentration changes in an attempt to trap the intermediates. The use of a chromium salt which would bind the complex tighter, might perhaps, change the rate of reaction. The reaction might be followed polarographically at the higher temperatures (25°). Conductivity measurements could give us a possible insight into the nature of the rust complex.

After establishing the kinetics of the reduction of phenylpropiolic acid in acidic media, the scope of the reduction might be broadened by experimentation with different phenylpropiolic acids, to determine if there is any Hammett ρ - σ relationship.

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